

High-order jamming crossovers and density anomalies

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We demonstrate the existence of high-order jamming crossovers in systems of particles with repulsive contact interactions, which originate from the collapse of successive coordination shells. At zero temperature, these crossovers induce an anomalous behavior of the bulk modulus, which varies non-monotonically with the density, while at finite temperature they induce density anomalies consisting in an increased diffusivity upon isothermal compression and in a negative thermal expansion coefficient. We rationalize the dependence of these crossovers on the softness of the interaction potential, and relate the jamming crossovers and the anomalous diffusivity through the investigation of the vibrational spectrum.

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Repulsive potentials with a finite range are investigated in a variety of different contexts, including the jamming transition of non thermal systems, and density anomalies of complex liquids. In the first case, these potentials are considered as models for the interaction between soft particle systems such as emulsions, bubble rafts and granular materials, which are not affected by Brownian motion. These systems undergo a jamming transition marking the onset of mechanical rigidity when the volume fraction crosses a threshold ϕ_J . See Refs. [1, 2] for recent reviews. At the jamming transition each particle is forced to touch particles in its first coordination shell, and the mean contact number per particle jumps to the isostatic value Z_{iso} , which is the minimum value required for mechanical stability. Above ϕ_J the excess contact number $\Delta Z = Z - Z_{\text{iso}}$ grows as a power law in $\phi - \phi_J$, and is related to a length scale diverging at the transition as ΔZ^{-1} , known as isostatic length. The jamming transition is characterized by an abundance of soft vibrational modes: the density of states $D(\omega)$ satisfies Debye scaling up to a characteristic frequency scaling as $\omega^* \propto \Delta Z$, above which $D(\omega)$ flattens.

Similar potentials, and in particular repulsive potentials with a cutoff distance D and with a smaller hard-core radius, are also commonly investigated at finite temperature to reproduce the density anomalies of water and of some other network-forming liquids. See Ref. [3] for a recent review. A density anomaly is a region of the phase diagram where the diffusivity increases upon isothermal compression, which usually overlaps with a region characterized by a negative thermal expansion coefficient. In network-forming liquids, these anomalies are related to soft vibrational modes characterized by a rigid rotation of tetrahedral structures, known as rigid unit modes [4]. Even though an abundance of soft modes characterizes both the jamming transition and the density anomalies, these two phenomena have not been related before, possibly because density anomalies occur at volume fractions well above ϕ_J [5–9].

In this Letter we show that the jamming transition is the first of a series of high-order jamming crossovers. These occur on increasing the volume fraction as particles are forced to make contact with those of subsequent coordination shells. The geometrical signatures of the jamming crossovers are oscillations in the rate of formation of new contacts on compression. The mechanical ones include an anomalous volume fraction dependence of the elasticity of the system, whereby the bulk and shear moduli vary non-monotonically with volume fraction. We show that density anomalies are the finite temperature counterpart of the jamming crossovers, and clarify the relation between these phenomena via the study of the soft vibrational modes.

Model – We perform Molecular Dynamics simulations of 50:50 binary mixtures of particles with diameter $D_l = 1$ and $D_s = D_l/1.4$ and mass $M = 1$. Two particles i and j interact if they have a positive overlap, $\delta_{ij} = D_{ij} - r_{ij} > 0$, where D_{ij} is their average diameter, and r_{ij} their distance. When this is the case the interaction potential is

$$V(r_{ij}) = \frac{1}{\alpha} k \left(\frac{\delta_{ij}}{D_l} \right)^\alpha, \quad (1)$$

where the parameter α controls the softness of the interaction potential, larger values of α corresponding to softer potentials. M , D_l and $k = 1$ are our units of mass, length and energy. Finite temperature simulations have been performed in the NVT and NPT ensembles, considering systems of $N = 10^3$ particles. Zero temperature properties have been investigated by quenching random configurations of $N = 10^4$ particles to the closest energy minimum via the conjugate-gradient algorithm [10]. We have considered a large volume fraction range, varying from the jamming threshold $\phi \simeq \phi_J$ ($\phi_J \simeq 0.84$ in 2d, $\phi_J \simeq 0.64$ in 3d) up to $\phi = 3$, and considered the following values of α : $\alpha = 1.25, 1.5$ (Hertzian), $1.75, 2$ (Harmonic), 2.5 and 3 . The $\alpha = 1$ case corresponds to the Jagla potential with

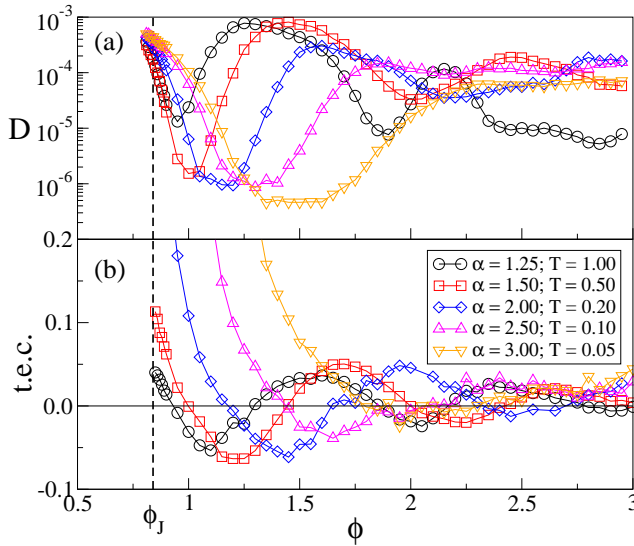


FIG. 1: (color online) (a) Volume fraction dependence of the diffusion coefficient averaged over the two species, for different interaction potentials. For each potential, the temperature is chosen so that the minimum value of D in the range of ϕ studied here is $D \simeq 10^{-6}$. (b) Thermal expansion coefficient.

no hard-core repulsion [5]. We report in the following results of 2d systems; analogous results hold in 3d.

T > 0 properties – We start by showing that systems of particles interacting via purely repulsive finite range potentials are not characterized by a single density anomaly as previously reported [5–9, 11], but by a series of successive density anomalies. Indeed, as illustrated in Fig. 1a, there exist successive volume fraction ranges in which the diffusivity increases upon isothermal compression. An analogous result has been observed in models of polymer stars [12]. Likewise, Fig. 1b shows the existence of multiple volume fraction ranges characterized by a negative thermal expansion coefficient. The diffusivity anomalies depend on the interaction potential: while for soft potentials (large α) a single anomaly is observed, more anomalies are observed on increasing the stiffness of the interaction. Likewise, the potential influences the number and the strength of the anomalies in the thermal expansion coefficient. In the following, we clarify the microscopic origin of these anomalies, and show that they are the finite temperature counterparts of high-order jamming crossovers.

T = 0 properties – We have investigated the volume fraction dependence of geometrical and mechanical properties of jammed configurations in a large volume fraction range. To this end we have considered volume fractions with a spacing of $\Delta\phi = 5 \cdot 10^{-2}$ far from the jamming transition and $\Delta\phi = 10^{-2}$ close to it; data are averaged over 50 independent jammed configurations for each value of ϕ . Measurements taken at volume fractions differing by $\Delta\phi$ have been used to estimate volume frac-

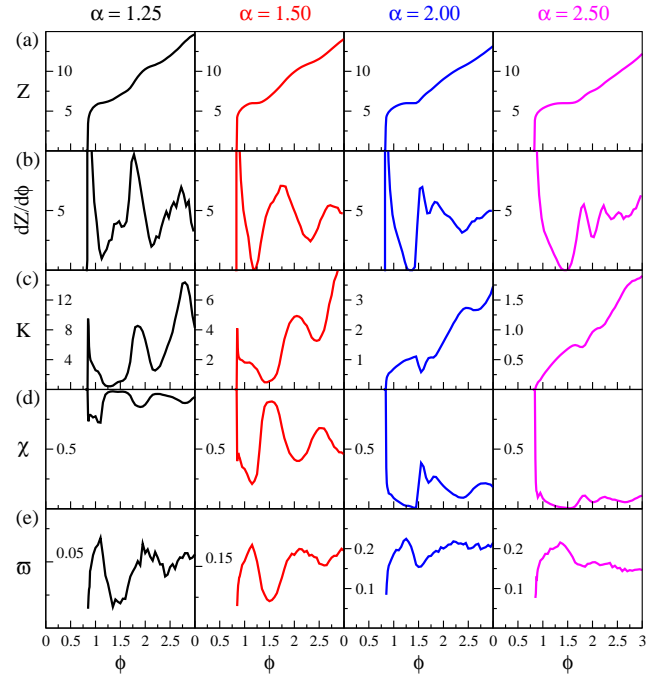


FIG. 2: (color online) Volume fraction dependence of the mean contact number Z (a), of its volume fraction derivative $dZ/d\phi$ (b), of the bulk modulus K (c), of the non affinity parameter χ (d), and of the normalized characteristic frequency ϖ (e). Each column refers to a different α value, as indicated.

tion derivatives numerically [13]. Figs. 2a,b illustrate the volume fraction dependence of the mean contact number and its first derivative. At the jamming transition, Z jumps to the isostatic value, while at higher volume fractions it grows with superimposed oscillations. Consistently, $dZ/d\phi$ diverges at the jamming transition, and then varies in an oscillating manner. As the divergence of $dZ/d\phi$ at the jamming transition corresponds to the collapse of the first coordination shell, the successive volume fraction ranges in which $dZ/d\phi$ increases can be interpreted as high-order jamming crossovers, during which each particle gradually makes contact with neighbors in successive coordination shells. In line with the fact that the shell structure is lost at high density, the crossovers become smoother as the volume fraction increases, and eventually Z increases linearly with ϕ . As an aside we note that for soft potentials there is a volume fraction range in which the average contact number is constant, $Z = 6$; here all particles in contact are Voronoi neighbors, and the value $Z = 6$ is fixed by Euler’s theorem for planar graphs. The jamming crossovers also influence mechanical properties such as the bulk modulus K , whose volume fraction dependence is shown in Fig. 2c. The effect of the crossovers on K depend on α . Indeed, minima and maxima of K and $dZ/d\phi$ are closely correlated for small α , and become less correlated as α increases, indicating that the smaller α , the greater the influence of the new

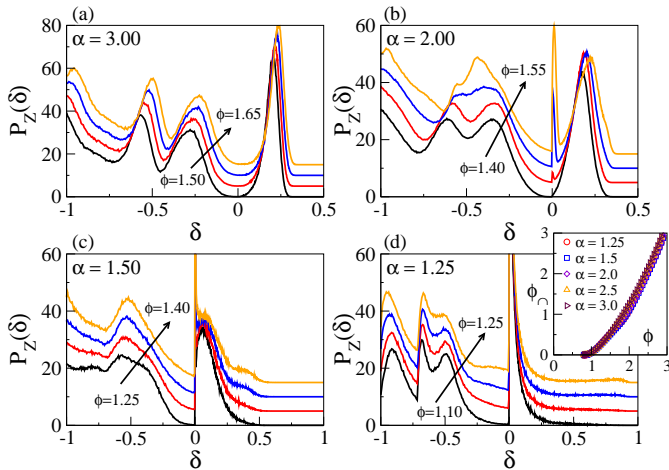


FIG. 3: (color online) Panels a,b,c: overlap probability distribution function $P_Z(\delta)$ for different values of the volume fraction separated by $\Delta\phi = 5 \times 10^{-2}$, as indicated. Data are shifted vertically for clarity. A negative δ corresponds to the distance between the surfaces of non-interacting particles. The inset of panel (d) shows that the intersection volume fraction ϕ_\cap is to a good approximation independent on the softness of the interaction α , specified in the legend.

contacts on the properties of the system. We finally note that the results of Fig. 2 do not support the conjecture of a transition at a volume fraction $\phi_d > \phi_J$ [14].

We elucidate the microscopic evolution of the system at the jamming crossovers investigating the volume fraction dependence of the overlap p.d.f. $P_Z(\delta)$, normalized across the interacting particles so that $\int_0^1 P_Z(\delta) d\delta = Z$. For monodisperse particles P_Z is fully equivalent to the radial distribution function. Since $dZ/d\phi$ increases when particles start interacting with those of a new shell, we show in Fig. 3 $P_Z(\delta)$ at volume fractions immediately following that of the first minimum of $dZ/d\phi$, for different values of α . For $\alpha = 3$ the making of new contacts does not strongly affect the distribution. $P_Z(\delta)$ is simply shifted towards larger values of δ , which suggests the presence of a mostly affine deformation. For $\alpha = 2$, on the other hand, the formation of new contacts leads to a transformation of $P_Z(\delta)$, whose net outcome is the creation of a new peak at small positive δ . This peak shifts towards positive δ values on further compressing the system. At smaller α , $P_Z(\delta)$ has a diverging peak at $\delta \rightarrow 0^+$, and the transformation of the distribution driven by contact formation leads to an increase of this peak. The higher order jamming crossovers lead to analogous changes in $P_Z(\delta)$. These results clarify that the jamming crossovers lead to a rearrangement of the force network of the system, which is more pronounced the smaller α . In particular, we note that that on increasing the volume fraction the shell structure observed in $P_Z(\delta)$ for $\delta < 0$, is transformed into a shell structure for positive overlaps for large α , while conversely it is washed

out for smaller α .

To explain the role of the softness of the interaction potential in the shape of the overlap probability distribution, we introduce the concept of intersection volume fraction ϕ_\cap . We define ϕ_\cap as the sum of the volumes of intersection of any pair of interacting particles, normalized by the total volume of the system. Close to the jamming transition, where the intersection volumes do not overlap, $\phi = \phi_J + \phi_\cap$, so ϕ_\cap is linearly dependent on ϕ and potential independent. In addition, here $\phi_\cap(\phi)$ scales as the q -th moment of $P_Z(\delta)$, $\phi_\cap \propto \langle \delta^q \rangle$, as the volume of intersection of two particles grows as δ^q for small δ , where $q = 1.5$ for $d = 2$ ($q = 2$ for $d = 3$). Fig. 3d (inset) shows that ϕ_\cap is also approximately potential independent at higher volume fractions, so we can regard it as being fixed by ϕ throughout. The energy of the system, on the other hand, scales as the α -th moment of $P_Z(\delta)$, $E \propto \langle \delta^\alpha \rangle$. Accordingly, constant- ϕ energy minimization protocols search for a P_Z distribution that minimizes $\langle \delta^\alpha \rangle$ subject to the constraint of constant $\langle \delta^q \rangle$, or to related constraints away from jamming. The effect of α on the outcome can be understood by considering the energy $e(\delta_i) = (\delta_i^\alpha + \delta_j^\alpha)/\alpha$ of two overlaps δ_i and δ_j related by the constraint of constant intersection volume fraction, $\delta_i^q + \delta_j^q = \text{const}$. Then for $\alpha > q$ it is energetically more favourable for the system to make the overlaps equal, while for $\alpha < q$ the energy is minimized by making them maximally different. This finding explains the abundance of small contacts in the overlap distribution for small α , and the qualitative change in P_Z as α crosses q .

The α dependence of the overlap distribution indicates that, the stiffer the interaction potential, the more heterogeneous the structure of the system. This suggests an increase of the non-affine response of the system on decreasing α . We estimate the degree of affinity of the system by comparing the actual bulk modulus K with that computed in the affine (Born) approximation, K_{aff} . If the system responds affinely to the compression, then $K = K_{\text{aff}}$, otherwise $K < K_{\text{aff}}$. Accordingly, the strength of the non-affine response, i.e. the relevance of the fluctuation term of the stress tensor [15], can be quantified via the parameter

$$\chi = \frac{K_{\text{aff}} - K}{K_{\text{aff}} + K}, \quad 0 \leq \chi \leq 1.$$

Then $\chi = 0$ when the response is affine, while $\chi \rightarrow 1$ when the response is highly non-affine. Fig. 2d confirms the expectation that stiffer potentials give rise to a less affine response, as the typical value of χ decreases on increasing α . In addition, the comparison of Figs. 2c and 2d reveals the presence of a clear anticorrelation between χ and K , which indicates that the jamming crossovers induce an increase of the degree of non-affinity of the system, much like the jamming transition. We also note that the oscillations of $\chi(\phi)$ suggest that the non-affine

correlation length that diverges at the jamming transition [1, 2] is a non-monotonic function of the volume fraction.

Connecting $T = 0$ and $T > 0$ – The mechanical anomalies observed at $T = 0$, and the dynamical ones observed at $T > 0$, have a closely related volume fraction dependence. This suggests that they have the same physical origin. We elucidate this mechanism by exploiting recent results correlating the thermal [16] and shear [17, 18] induced relaxation of glassy systems, and their vibrational modes. These studies have shown that the relaxation proceeds through localized events, which occur where the low frequency modes are quasi-localized. In this picture, low-frequency modes are defects allowing for the relaxation of disordered particle systems [18]. In particular, since the activation energy of a soft mode is correlated with its eigenfrequency [19], one expects the dynamics to speed up when the typical frequency of the soft modes decreases. We have checked this expectation by studying the volume fraction dependence of the average eigenfrequency ϖ of the lowest modes (5%), normalized by the average eigenfrequency of all modes. Results are illustrated in Fig. 2e, for different interaction potentials. ϖ exhibits oscillations as the volume fraction increases, which are anti-correlated with those of the diffusion coefficient. In addition, ϖ is also strongly anti-correlated with the parameter χ . These results confirm the important role of the soft modes in determining both the relaxation dynamics as well as the mechanical properties of the system.

Conclusions – We have demonstrated the existence of high-order jamming crossovers in soft particle systems with increasing density. These occur when particles start to touch neighbors in subsequent coordination shells. The mechanical manifestation of these crossovers is the anomalous behavior of elastic properties such as the bulk and the shear (data not shown) moduli, which vary non-monotonically with the volume fraction. Their dynamical manifestation are density anomalies, which include both an increased diffusivity on compression and a negative thermal expansion coefficient. We have related the $T = 0$ and the $T > 0$ anomalies to the emergence of soft vibrational modes in correspondence with the crossovers, confirming their important role in the relaxation dynamics [16–18]. These results suggest that the scaling relation between relaxation time and vibrational dynamics found in normal liquids [20] may also hold for anomalous liquids. We finally note that the anomalies are observed at the high-order jamming crossovers, and not at the jamming transition, where the diffusion coefficient decreases monotonically on compression. One may speculate that this is so because at the jamming crossovers there is a coexistence of compressed bonds, and of new almost uncompressed bonds. These bonds may play the role of the two interaction length scales which are known to induce dynamical anomalies in models of water [3],

and are responsible for the rigid unit modes leading to a negative thermal expansion coefficient in network forming systems [4]. These two length scales are not present at the jamming transition. In this respect, it would be interesting to investigate the spatial structure of the soft modes at the jamming crossover.

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